



U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Fuel Cycle Research and Development

**Historical and Current Crucible
Materials and the Effects on Processing**

Randall Fielding, Ken Marsden, Dr. Ki-Hwan Kim*
Idaho National Laboratory

*** Korean Atomic Energy Research Institute
(KAERI)**

**2012 International Pyroprocessing Research
Conference**

Aug. 26 – Aug. 30, 2012



U.S. DEPARTMENT OF
ENERGY

Outline

Nuclear Energy

- **Introduction**
- **Historical Coatings**
- **Current Coatings in pyroprocessing and fuel fabrication**
- **Conclusions/Future Plans**



Introduction

Nuclear Energy

- **Uranium melts are quite reactive and will react with many commonly used crucible materials**
- **U-Zr melts are more reactive and further react with common crucible materials**
 - Reduces many crucibles (oxides and others)
 - Dissolves graphite materials
- **Coatings are used to protect the crucible from interaction and in some cases from wetting by the melt**
- **Common crucible or coatings include:**
 - Y_2O_3
 - ZrO_2
 - ThO_2
 - MgO
 - Er_2O_3
 - Others
- **Goal- To produce a coating that is non-reactive and is re-useable or can be efficiently applied remotely**



U.S. DEPARTMENT OF
ENERGY

Experience

Nuclear Energy

- **EBR-II 1964-1969 – Fuel Demonstration Project**
 - Melt refining followed by fuel fabrication

- **EBR-II 1984-1994 – Integral Fast Reactor**
 - Pyrometallurgical separations followed by fuel fabrication

- **EBR-II Fresh Fuel Fabrication- multiple time periods after the Fuel Demonstration Project**

- **Advanced separations and fuel fabrication research – Present**
 - Processing of spent EBR-II fuel
 - FCRD research (separations and fuel)



Fuel Demonstration Project

Nuclear Energy

- **Fuel Fabrication-** casting was done in a graphite crucible coated with $\text{ThO}_2\text{:ZrO}_2$ (95:5)
 - Molds also coated with ThO_2
 - Later a switch was made to ZrO_2 - good performance w/o contamination concerns

- **Melt Refining-** Used fuel is melted allowing volatile elements to volatilize off, more reactive element such as rare earth, alkali, and alkaline earth react with the crucible to form a slag
 - Coatings were not used because interaction was needed
 - Melt would partially reduce crucible and form a slag on top and sides of the crucible

- **Several crucible materials were investigated for melt refining and were found to be effective: graphite, Al_2O_3 , ZrO_2 , ThO_2 , BeO**
 - CaO stabilized ZrO_2 was used in the hot cell
 - *Better Cs separation and higher pouring yields*



Fuel Demonstration Project

Nuclear Energy

	Skull	Crucible	Ingot
U	5-10%	---	90-95%
Pu	5-10%	---	90-95%
Noble Metals	5-10%	---	90-95%
Y	95%	5%	---
Rare Earth	95%	5%	---
Ba	10%	90%	---
Sr	10%	90%	---
Te	90%	10%	---

Skull- Oxide dross which floats on the melt and adheres to the crucible walls

Crucible- Elements which diffuse into the crucible wall

Ingot- Metal ingot that can be poured from the crucible



Fresh Fuel Fabrication

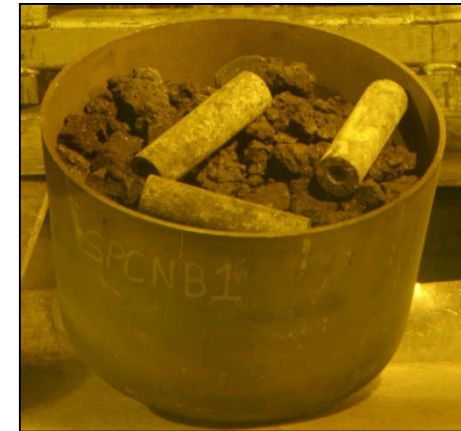
- EBR-II fresh fuel fabrication includes both U-5Fs and U-10Zr fuels
- U-5Fs alloying was done in a CaO stabilized ZrO_2 crucible
- Fuel Casting was done in a Y_2O_3 wash coated graphite crucible
 - Coating would be removed (wire brushing or scraping) and re-applied each run
- Molds were wash coated with ZrO_2
 - Y_2O_3 wash coating were investigated but the fuel slug surface finish suffered
 - *It is thought that this was due to the Y_2O_3 being water based while the ZrO_2 was ethanol based*



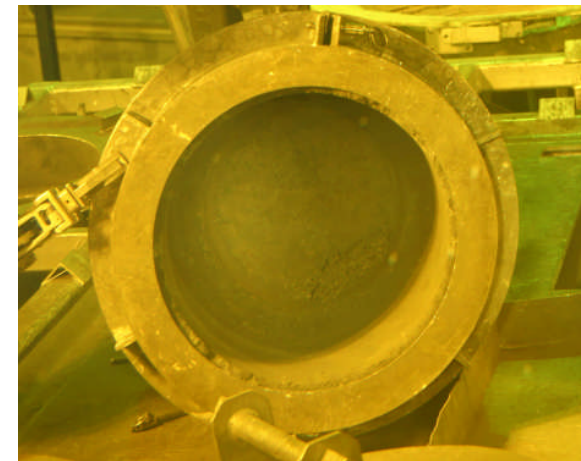
Current Pyrochemical Recycling

■ Cathode Processing

- A challenging environment, where compatibility with both U metal and UCl_3 -bearing salts at very high temperature is necessary
- In processing of U-10Zr fuel, carryover of several % of zirconium may occur in some processing conditions, which adds another level of melt reactivity
- ZrO_2 has *moderate* resistance to both metallic U and UCl_3 , and selected as a compromise
- Traditional approach was thick coating of ZrO_2 on graphite, but crucible cleaning, recoating, and pre-firing of the coating were laborious
- HfN-coated Nb held some promise – but found incompatible with zirconium carryover
- Current technology is composite crucible, a graphite shell for handling strength, with ZrO_2 ceramic lining for resistance to dendrite product
 - Avoids labor of single-use coating
 - Crucible lifetime increased



6-Liter HfN-coated test crucible



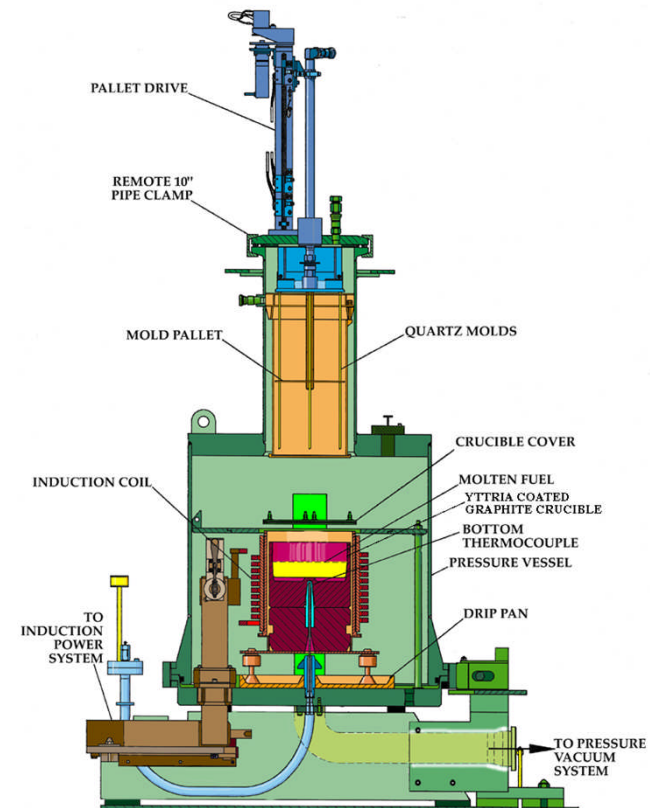
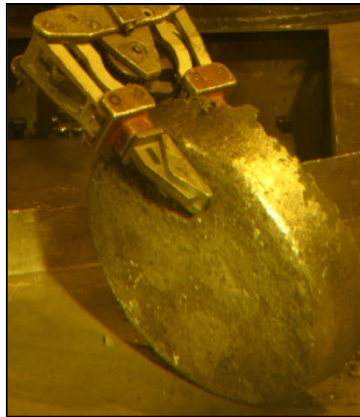
ZrO_2 -lined graphite crucible



Current Pyrochemical Recycling

■ Casting

- Excellent performance of commercially-available Y_2O_3 coating
- Salt species are already removed, so less complicated environment
 - *If they are not, Y_2O_3 coating will be penetrated, with resulting high carbon content in ingot and potential crucible destruction upon ingot removal*
- Low losses and ease of use of Y_2O_3 coating have limited efforts to replace coating with permanent material





Other Possibilities

Nuclear Energy

- **A lot of research has been done in this area**
 - Many tests have been somewhat conservative or have been overly aggressive
- **Test were done with 100% uranium at 1300°C - 1600°C**
- **Test were done with 100% zirconium at 1787°C - 2212°C**



Other Possibilities

Nuclear Energy

1997	S. McDeavitt	ZrN	U	1605	Poor melting	Severe reaction
1997	S. McDeavitt	HfN	U	1605	Poor melting	No reaction
1997	S. McDeavitt	ZrC	U	1412	GB attack	
1997	S. McDeavitt	HfC	U	1412	Infiltration	No rxn!!
1997	S. McDeavitt	4TaHf-Carbide	U	1412	Wetting	Rxn; 90° CA
1997	S. McDeavitt	Ta-Ta ₂ C	U	1412	Wetting	Bonded; 25° CA
1997	S. McDeavitt	TiN	U	1411	Non-wetting	Rxn, layer
1997	S. McDeavitt	Y ₂ O ₃	U	1411	Non-wetting	Release
1997	S. McDeavitt	MgO	U	1411	Rxn.	
1997	S. McDeavitt	TiC	U	1411	GB attack	
1997	S. McDeavitt	BeO	U	1510	Non-wetting	Release
1997	S. McDeavitt	MgZrO ₃	U	1510	Non-wetting	Release
1997	S. McDeavitt	CaZrO ₃	U	1510	Non-wetting	Release
1997	S. McDeavitt	CaHfO ₃	U	1510	Non-wetting	Release
1997	S. McDeavitt	Hf-HfN	U	1325	Wetting	Rxn at 1320°C
1997	S. McDeavitt	W	U	1325	Melt/spread at 1177°C	
1997	S. McDeavitt	YAG	U	1325	Non-wetting	No rxn.
1997	S. McDeavitt	MgAl ₂ O ₄	U	1325	Non-wetting	Release
1978	C.E.Holcombe (Y-12)	TiN	U	1600	Reacted with U above 1407°C	TiN, UN, UO ₂
1978	C.E.Holcombe (Y-12)	HfC	U	1600	No significant reaction	No U compounds
1978	C.E.Holcombe (Y-12)	CeS	U	1600	No significant reaction	No U compounds
1978	C.E.Holcombe (Y-12)	Ce ₂ S ₃	U	1600	No significant reaction	No U compounds



Other Possibilities

Nuclear Energy

2001	S. McDeavitt	ZrN	Zr	2212	Zr did not melt at 1855°C, but at 1975°C (N from ZrN reacted with pure Zr)	Intensive reaction/strong bonding, ZrN _(1-x) formation (~40μm)
2001	S. McDeavitt	HfN	Zr	2212	Melt at ~2100°C (N contamination from HfN of Zr metal)	Intensive reaction. ZrN _(1-x) formation (100μm). (HfN _(s) +Zr _(s) =>HfN _(1-x) +aZrN _(1-x'') +bZr(α) _N +cN ₂)
2001	S. McDeavitt	Hf ₂ N	Zr	2212	Intensive interaction, ZrN _(1-x) formation	
2001	S. McDeavitt	ZrC	Zr	1910	Melt at ~1910°C	<u>No chemical reaction</u> <u>(Clean/Smooth ZrC surface),</u> <u>No transition phase</u>
2001	S. McDeavitt	Y₂O₃	Zr	~2000	3Zr _(s) + Y ₂ O _{3(s)} = 3Zr(O) + 2Y Y decreases Zr melting point	<u>Strong bonding,</u> <u>No transition phase</u>
2000	S. McDeavitt	HfC	Zr	2000	<u>No chemical reaction/some interface reaction</u> <u>No transition phase</u>	
2001	S. McDeavitt	BeO	Zr	2000	Significant/severe reaction at 1550°C	
1995	S. McDeavitt	ZrB ₂	Zr	2212	Severe reaction at ~1700°C	
1995	S. McDeavitt	HfB ₂	Zr	2212	Severe reaction at 1540°C	
1995	S. McDeavitt	Ta-Ta ₂ C	Zr	1935	Spreading; reaction	
1995	S. McDeavitt	Ce _x S _y	Zr	1787	Sample melted at 1550°C	
1995	S. McDeavitt	Ce ₂ S ₃	Zr	1787	Sample melted at 1550°C	
1995	S. McDeavitt	MgO	Zr	1787	Solid-solid reaction	



Experimental Results

- **HfN, TiC, ZrC, and Y₂O₃ were plasma sprayed onto 6.35 mm diameter Nb rods**
 - Vacuum/inert plasma spraying was not possible
- **XRD and SEM/EDX analysis did show oxide contamination on HfN, TiC, and ZrC**
- **Samples were exposed to U-20Zr (weight percent) at 1550°C for 5 minutes followed by cooling in the melt**
- **Microstructurally characterized**

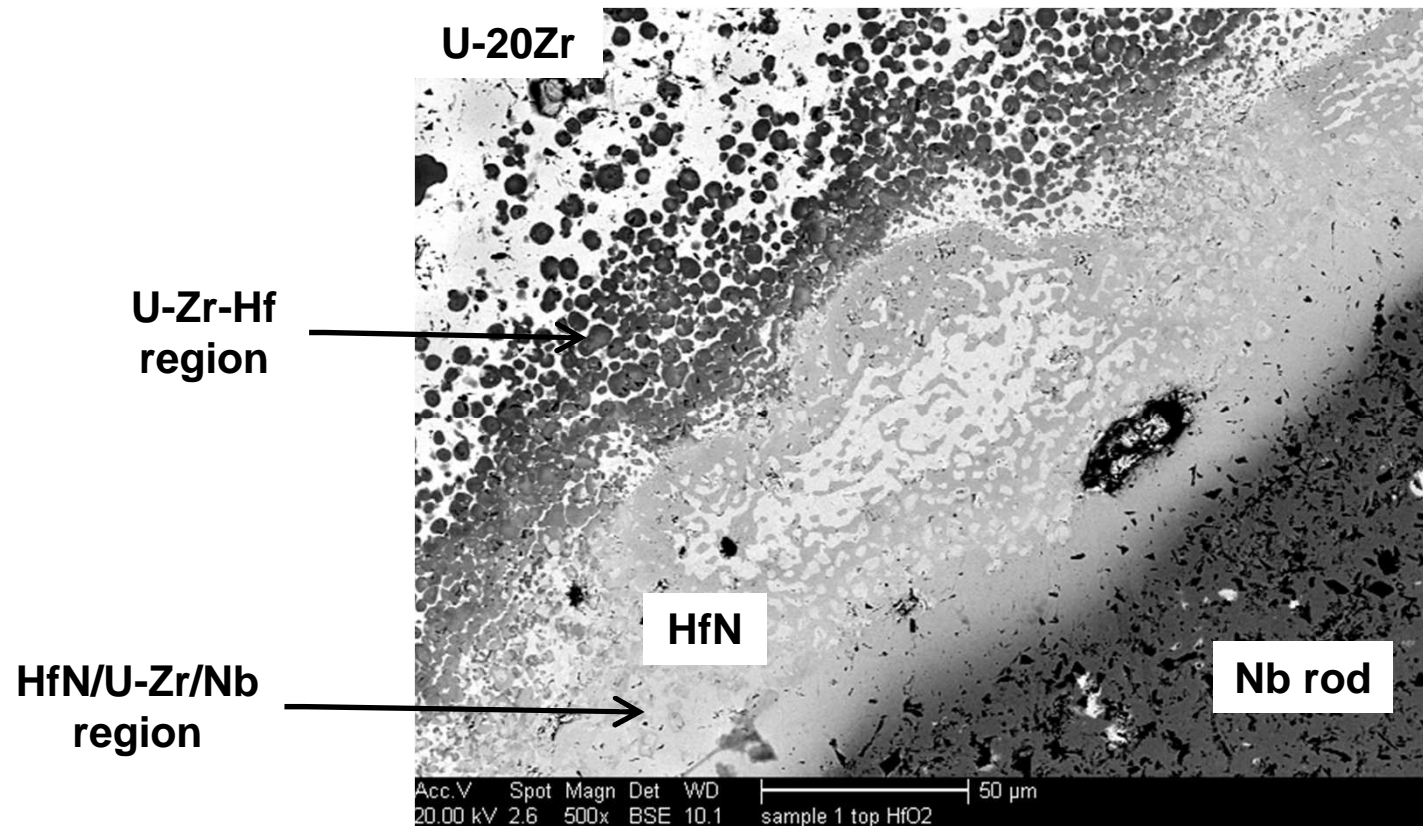




U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Experimental Results-HfN



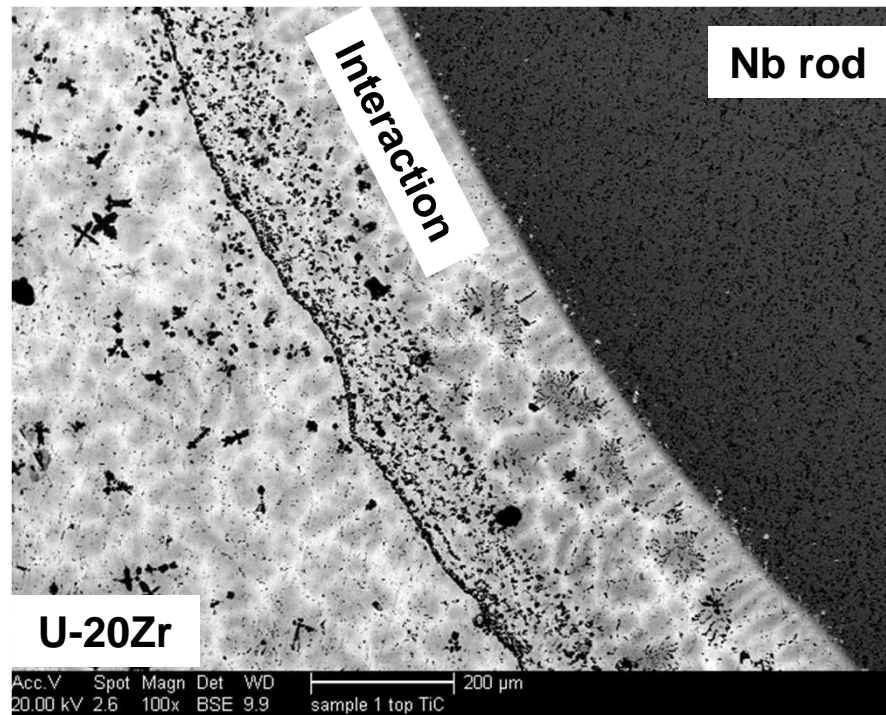


U.S. DEPARTMENT OF
ENERGY

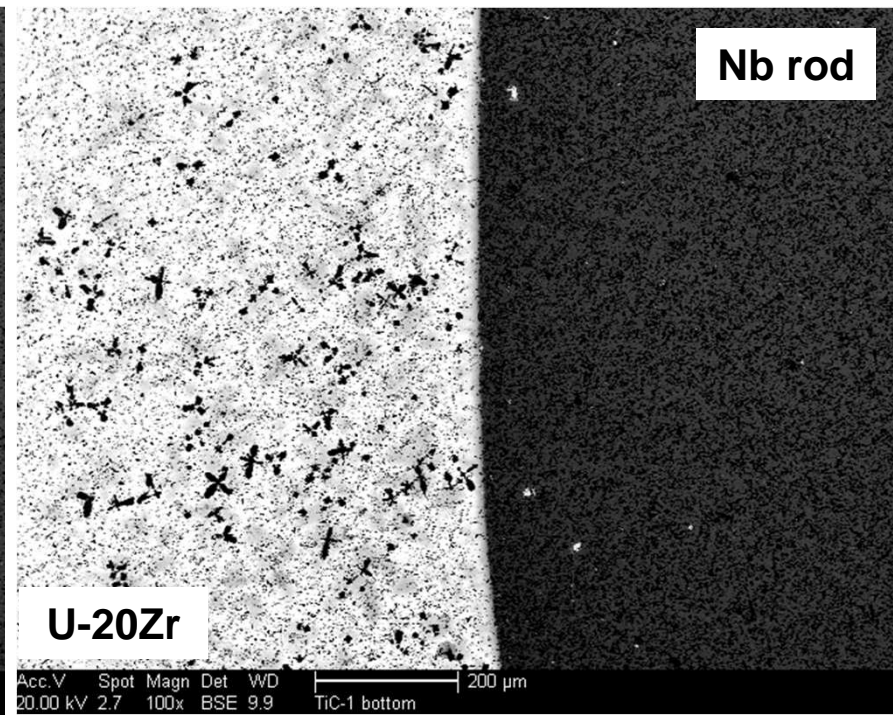
Nuclear Energy

Experimental Results- TiC

Towards top of melt



Towards bottom of melt

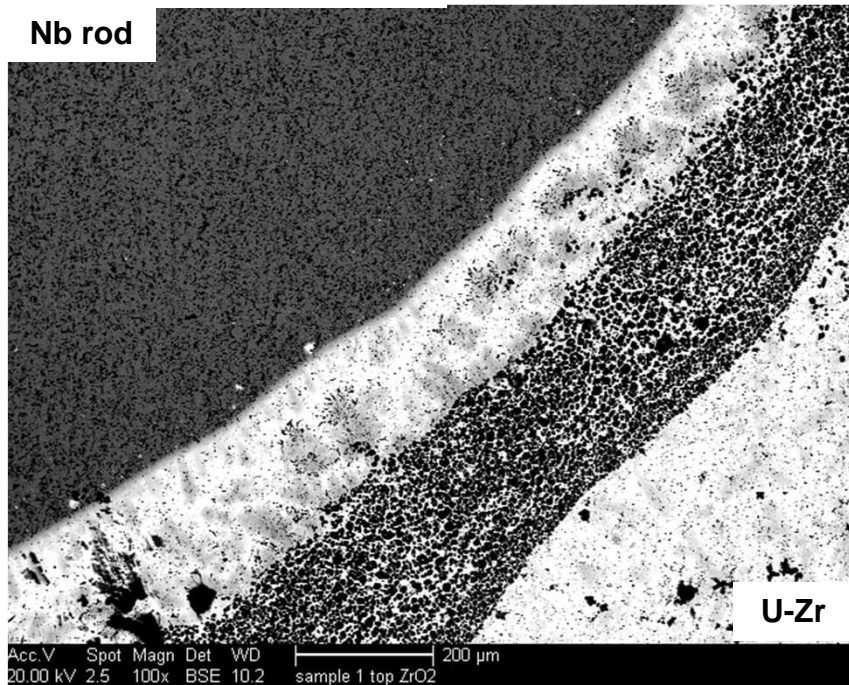




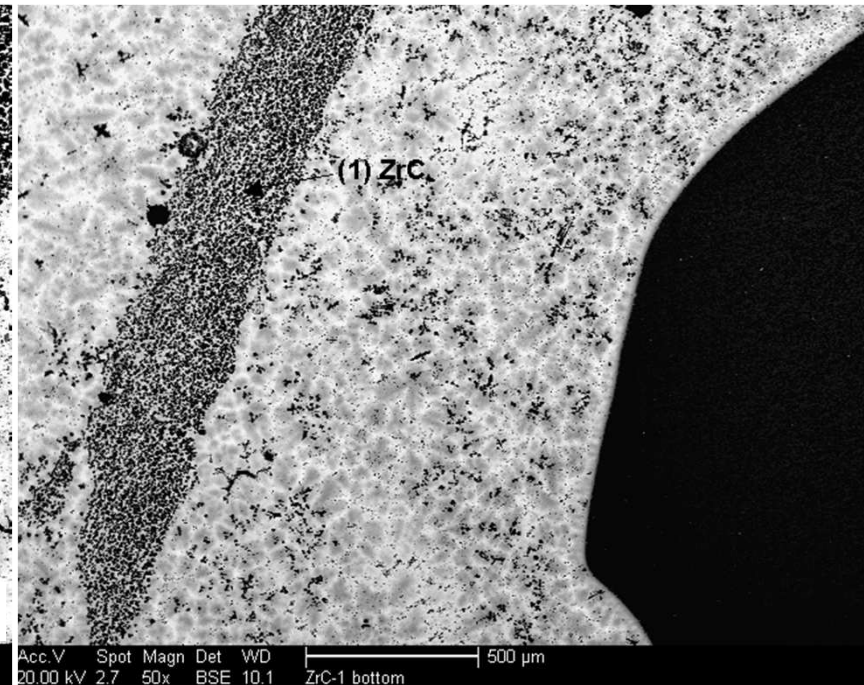
Experimental Results- ZrC

Towards top of melt

Nb rod



Towards bottom of melt

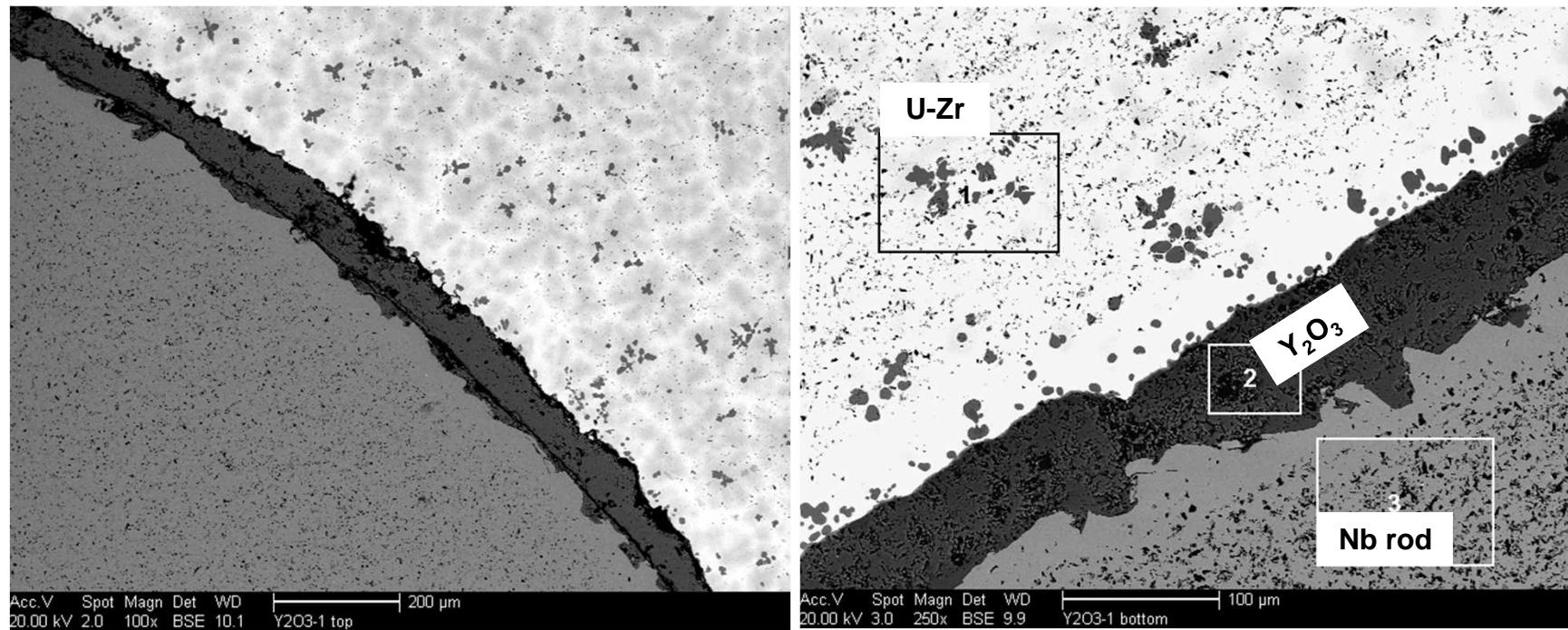




U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Experimental Results- Y_2O_3





- **Coatings are important for clean melts and can be a source of fuel losses throughout the fuel cycle**
- **Y_2O_3 is an effective coating for limiting melt/crucible interaction however mechanical and adhesion properties can be an issue**
 - Frequent re-coating
- **Coating method may play an important role in coating interaction**
 - Vacuum vs. non-vacuum for more reactive materials
- **More work is needed to identify a more robust coating**
 - Currently most research has focused on U and U-Zr alloys- recycled fuel may contain reactive lanthanide that may react with the coatings and subsequently the crucible
 - *Sm volatility experiments- Y_2O_3 was reduced by Sm creating much more crucible/melt interaction*
 - *Alloying agents, i.e. Zr, affect how well the coatings protect the crucible*
- **Coatings must be evaluated against the process to be used**
 - Bottom or tilt pour crucibles may be able to withstand some wetting



- **More complex coatings-** majority of materials that have been studied have been binary compounds-
- **Novel coatings-** melt refining dross was stable in the U-Fs melts this may be a starting place for a more robust coating for recycled U-Zr fuels
 - UO_2 coatings- oxide layers or rafts are common in melts, these may also be utilized for new coatings
- **Disposal crucibles-** bare refractory crucibles that can be directly recycled through the pyroprocess?
- **Coating application development (CVD, PVD, plasma spray, laser deposition, etc.)**